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<b>(21) International Application Number:</b> PCT/US96/06518 <b>(22) International Filing Date:</b> 8 May 1996 (08.05.96)  <b>(30) Priority Data:</b> 08/440,412 12 May 1995 (12.05.95) US  <b>(71) Applicant:</b> CHEM PRO LABORATORY, INC. [US/US]; 941 West 190th Street, Gardena, CA 90248-4398 (US). <b>(72) Inventors:</b> SYDER, Milton, W.; 243 18th Street, Santa Monica, CA 90402 (US). BORTNIK, Michael; 1107 1/2 18th Street, Santa Monica, CA 90403 (US). <b>(74) Agents:</b> GRAY, Arthur, D. et al.; Kenyon & Kenyon, One Broadway, New York, NY 10004 (US).		<b>(81) Designated States:</b> CA, JP, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> With international search report.
<b>(54) Title:</b> CORROSION PRODUCTS REMOVAL METHODS AND COMPOSITIONS FOR USE THEREIN  <b>(57) Abstract</b> <p>A method is described for removing corrosion products formed <i>in situ</i>, transported corrosion products, iron staining from water, which resides on fixtures, and unwanted materials trapped within and/or in association with corrosion products from iron, steels, and copper, alloys of these metals and from other surfaces, specifically including glasses, plastics, elastomers, ceramics, tiles and porcelains. The method comprises contacting corroded surfaces and/or surfaces supporting corrosion products with an aqueous composition containing citric acid or its salts, at least one organophosphonate or its salts, and at least one water-soluble polymer or its salts. A corrosion inhibitor may be included in the composition. One or more alkali metal or alkaline earth metal or ammonium hydroxides may be included for adjusting the pH, and/or for controlling the kinetics of the removal method. Enhancements such as abrasives, coloring agents and odorizers may also be included.</p>		

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CORROSION PRODUCTS REMOVAL METHODS AND COMPOSITIONS  
FOR USE THEREIN

This invention relates to methods useful for removing various forms of corrosion products, either formed in situ, or transported, or deposits from boilers, cooling devices and non-contact heat exchange equipment (i.e., surface condensers and the like) and other aqueous fluid-containing apparatus, and from piping, fittings, valves, and ancillary apparatus employed in conjunction with them. The methods, and the compositions employed in them, are also useful in removing rust, rust stains and water-formed deposits ("scale") from industrial, commercial, municipal, agricultural, recreational, consumer and domestic apparatus, including non-metallic apparatus. Such use includes removing rust from industrial and domestic tools, kitchen appliances, and the like, and for removing rust stains from sinks and porcelain lavatory facilities. Such use also includes removing corrosion products, rust, stains, deposit and/or scales specifically from iron, steels and coppers, alloys of these metals and from glasses, plastics, elastomers, tiles, ceramics, porcelains, and other surfaces.

The methods and compositions described herein are useful in cleaning boilers, heat exchangers, piping, reaction vessels and other vessel watersides. Such apparatus is typically employed in boilers generating steam for use as such, or for generating electricity, or for reaction vessels employed, illustratively, in the refining, petrochemical, chemical, pulp and paper and steam electric generating industry including nuclear power plants, fossil fuel power plants and nuclear fuel processing facilities, and in a wide variety of waterside heating and cooling service duties. It is understood that both the steam and water involved may be utilized for heating purposes, cooling purposes or process purposes, either in direct contact service duty or in non-contact service duty.

The method, and the compositions, are also useful for down-the-hole cleaning of oil wells, in maintenance of heating, ventilating and air-conditioning apparatus of buildings, and the preparation of metal and other surfaces prior to painting or other surfacing.

Corrosion products occur in the form of oxides, hydroxides and other related forms of iron, copper, manganese, nickel, chromium, zinc, cobalt, and other deposits. These corrosion products and deposits tend to reduce the rate of flow of fluids through pipes and other conduits, clog valves, and reduce the rate of heat transfer through the walls of vessels and pipes, and often promote the advancement of one or more corrosion processes. In extreme cases, the corrosion also tends to reduce the effective thickness of the pipes and vessels, which can result in the formation of leaks or even physical rupture of a pipe or vessel. This is especially true if the normal operation is conducted at an elevated pressure, in which event a rupture of metal can be hazardous to people, as well as destroying parts of the apparatus and interrupting the operation of an industrial facility.

Common stages of corrosion can result in underdeposit corrosion, which increases the risk of severe localized corrosion, including among other results, the pitting of the walls of pipes and vessels, further increasing the risk of metal failure. The rate of underdeposit corrosion in water systems is often observed to be rapid. Furthermore, much of this corrosion results in the generation of localized, relatively deep pits rather than in relatively shallow generalized corrosion. This localized pitting corrosion tends to induce throughwall leaks faster than does generalized corrosion.

Broadly stated, the invention comprises methods for removing corrosion products and/or associated deposits from piping, fittings, tools, and vessels made of iron,

steel or copper, employing an aqueous corrosion removal composition comprising (A) citric acid, including partially neutralized citric acid; (B) at least one phosphonic acid or an organic salt thereof, said phosphonic acid or salt being characterized by ability to form sequestrates or complexates with iron and/or copper; and (C) at least one water-soluble polymeric composition, wherein at least five percent by weight of said water-soluble polymeric composition is derived from one or more of the monomers selected from the class consisting essentially of acrylic acid, methylacrylic acid, maleic acid, and/or acrylamide, said water-soluble polymeric composition having a weight average molecular weight in the range from about 500 grams per mole to about 500,000 grams per mole, and having the characteristic of dispersing particles of the products of the corrosion of iron, copper, including oxides, hydroxides and other metal derivatives as well as generic silts and the like.

The corrosion removal composition may also comprise sodium, potassium, ammonium hydroxide or other alkaline hydroxides in an amount sufficient to create a pH in the range of from about 6.5 to less than one in an aqueous concentrate of said corrosion products removal composition.

The corrosion products removal composition may also comprise a corrosion inhibitor having the characteristic of being effective to prevent corrosion attack on iron, steels, copper and their alloys.

Typically, the corrosion products removal concentrate composition comprises water, and in use is employed in an aqueous environment.

An important selection criterion for the phosphonic acid(s) or salt(s) to be employed is its or their ability to form a complexate and/or a sequesterate with oxides, hydroxides and other related forms of the corrosion products of iron or copper. The phosphonic acid or salt

is advantageously selected from the class consisting essentially of: 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP); diethylenetriaminepentamethylenephosphonic acid (DETPMP); ethylenediaminetetramethylenephosphonic acid (EDTMP);

aminotrimethylenephosphonic acid (AMP);

hexamethylenediaminetetramethylenephosphonic acid (HMDTMP); 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC); and hydroxy phosphonic acid (HPA).

1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) is a preferred organo-phosphonate for use in the corrosion products removal compositions. A commercial source of it is a solution comprising 40% water sold under the trade name MAYOQUEST 1500 by the Mayo Chemical Co., Inc., of Smyrna, Georgia.

An important selection criterion for the water-soluble polymeric composition is its ability to disperse particles of the corrosion products of iron or copper. The water-soluble polymer or polymers that may be employed include homopolymers, and copolymers of one or a plurality, of the monomers acrylic acid, methacrylic acid, maleic acid, and acrylamide. They also include co-, ter-, and tetra-(or quatra-) polymers of any of the foregoing monomers with other compounds, including one or more copolymerizable additional monomers containing at least one of an oxygen atom, a sulfur atom, a nitrogen atom or a phosphorous atom, or at least one alkyl group having up to 18 carbon atoms, including, illustratively, but not limited to, polymerizable sulfo-oxygen compounds and polymerizable phospho-oxygen compounds. Such copolymerizable additional monomers include an adduct or a derivative of the same. The water-soluble polymers also include terpolymers known as the acrylic acid/sulfonate/nonionic (AA/S/N) type.

The water-soluble polymeric composition may be of a narrower weight average molecular weight range, such as in the range of about 500 to about 200,000 grams per

mole. An advantageous range is from about 500 to about 6,000 grams per mole.

5 A preferred water-soluble polymer is polyacrylic acid, or a salt of it, having a weight average molecular weight of about 2,000. A commercial source of it is an aqueous solution comprising 50% water sold under the tradename J-POLY MW 200 by Johnson Polymers Co., Inc., of Manvel, Texas.

10 A corrosion inhibitor is desirably employed to prevent corrosion attack by citric acid or other components on non-corroded metal surfaces. Corrosion inhibitors are typically sold as proprietary products, the formulation (including the identity and relative amounts of the constituents) of which is generally not  
15 revealed by the manufacturer. Various types of corrosion inhibitors are described by George Gardner in a chapter entitled "Inhibitors In Acid Systems," pages 156 et seq., in a publication of NACE International, formerly the National Association of Corrosion Engineers (NACE),  
20 available in the Library of Congress, Catalog No. 73-85564.

25 A cationic or a cationic blend of nitrogen-containing compounds is a suitable corrosion inhibitor for metals cleaned by citric acid. An example of such an inhibitor is ethoxylated technical grade hydroabietylamine (63%), isopropanol (30%), and rosin amines (7%). It is available under the tradename POLYRAD 1110A from Hercules Incorporated, Wilmington, Delaware, for which see its Material Safety Data Sheet No. 856-  
30 2187-0800-04 dated September 3, 1993.

35 Another suitable corrosion inhibitor comprises 50-60% of a "complex substituted keto-amine," 10-15% isopropanol, 1-3% propargyl alcohol, 3-5% formaldehyde and 1-3% triphenyl sulfonium chloride, for which see the Material Safety Data Sheet dated March 16, 1987, of Amchem Products, Inc., a division of the Henkel

Corporation, Ambler, Pennsylvania, for its product sold under the tradename RODINE® 213.

The same manufacturer also sells a product under the tradename RODINE® 103. Its Material Safety Data Sheet states that it comprises about 1-3% phosphoric acid, (unidentified) phosphates and water, with a pH of about 2-3 (before dilution) and a specific gravity of about 1.1.

Sodium, potassium, ammonium hydroxide, or other alkaline hydroxides, may be employed sufficient to produce a pH of the final composition of 6.5 or less. Since in some methods of use, the corrosion products removal composition may be employed at a relatively low pH, even less than one, including when a hydroxide is not necessary. A suitable intermediate pH is in the range of from about 2-1/2 to about 4-1/2. A preferred pH is in the range of about 3 to about 3-1/2. However, for any given formulation the amount of hydroxide that is needed to produce a desired pH is not readily calculable, because of the complex chemistry of the compositions. The amount is especially dependent on the degree, if any, of partial neutralization of the citric acid employed, especially in view of the tricarboxyl structure of citric acid and the large fraction of the active ingredients in the composition represented by citric acid or its partially neutralized salts.

Desirable ranges of relative ratios, on a parts by weight basis and also on an anhydrous basis, of the several constituents of the corrosion removal composition, having a pH in the range of about 3 to 3-1/2, are stated in the following tabulation:

Citric acid, and/or its salts	from about	45	to about	75
A phosphonic acid and/or its salts	from about	2	to about	15

Water-soluble polymer and/or salts thereof	from about	1-1/2	to about	8
Sodium hydroxide	from about	8	to about	11
Corrosion inhibitor	from about	1	to about	4

In the event potassium hydroxide were to be substituted for sodium hydroxide, the relative weight ratios for it would be in the range of from about 11 to about 16.

In the event a specific corrosion removal composition is formulated without a hydroxide or a corrosion inhibitor, the relative range of proportions of the other constituents remains the same. Also, in the foregoing table, the ratios of the water-soluble polymer are expressed on an anhydrous basis, even though such polymeric compositions are frequently sold commercially as a solution comprising approximately 30% to 80% of water.

The amounts of the ingredients, exclusive of water, of a preferred corrosion products removal composition concentrate comprise about 58 weight percent technical grade citric acid, about 14% 1-hydroxyethylidene-1,1-diphosphonic acid, about 4% polyacrylic acid having a molecular weight of about 2000; sufficient potassium or sodium hydroxide, about 22% in compositions wherein the citric acid is partially neutralized, to create a pH in the range from about 3 to 3-1/2 in the final concentrate composition, including water, and about 2% of RODINE 103® as the corrosion inhibitor. Since the corrosion inhibitor formulation is usually not furnished by the manufacturer of the inhibitor, its weight percentage is stated on an as-sold basis.

When preparing corrosion removal compositions intended for industrial uses, it is convenient to formulate them as an aqueous corrosion products removal

concentrate, in which the amount of water is about 2 to about 3 parts by weight per one part of anhydrous constituents. Subsequent dilution may be made by the user.

5       The foregoing compositions may be prepared by conventional mixing procedures, optionally including stirring, at room temperature, below room temperature or at elevated temperatures.

10       When the method and a composition is to be employed to remove rust or copper corrosion products from domestic or industrial tools, kitchen appliances, and the like, or to remove rust stains or copper stains from kitchen sinks and porcelain lavatory facilities, the composition may be packaged in small containers suitable for retail sale in  
15       stores. For such purposes, and for some industrial or commercial uses, additional constituents may be included, such as one or more abrasives, disinfectants, odorizers, coloring agents, viscosity modifiers, and/or biocides.

20       As employed herein, the terms iron and steel include illustratively cast iron, ductile iron, carbon steel, and the several grades and types of stainless steels and iron-nickel alloys. The term copper includes alloys thereof, including illustratively, the cupronickels, alpha-brasses, beta-brasses and bronzes, including the  
25       aluminum bronzes and phosphorbronzes.

30       In commercial and/or industrial use, the methods may be employed in a recirculating system, or in a static system without recirculation, i.e., simply allowing the corroded surfaces, or the surfaces containing corrosion products, of the apparatus to soak in contact with the corrosion products removal composition. Generally, one volume of a corrosion products removal concentrate composition will be diluted within the range of from  
35       about 2 to about 20 to 30 volumes of water filling the apparatus to be cleaned. A generally preferred dilution ratio is one volume of a corrosion products removal concentrate composition to two to ten volumes of water.

The compositions are effective in removing corrosion products when employed at ambient temperatures, but may be employed at elevated temperatures if desired.

5 The time required to achieve the desired extent of removal of corrosion depends upon several factors and is not readily calculable in advance. Those factors include the concentration of the composition that is in contact with the corroded metal surface or the surface containing corrosion products, the surface area of contact, the  
10 turnover of fresh chemical composition, the temperature employed, the severity of corrosion, i.e., the quantity and the condition and the composition of the corrosion products with or without other materials, the pH of the fluid in contact with a corroded or corrosion product-containing surface, and also the extent of the desired  
15 completeness of removal of corrosion products.

Properly employed with regard to the foregoing, the methods and compositions described herein are capable of removing up to virtually 100% of the corrosion products  
20 in pits, even in deep pits, or in occluded and near-occluded cavities formed by the corrosion of metal, the fabrication of the system, or general geometry of the components of the system in contact with a corrosion products removal composition. This feature has a  
25 substantial advantage when corrosion has progressed to the point where the products of corrosion have accumulated in deep pits in the metal. This feature additionally has a substantial advantage when corrosion product accumulations tend to facilitate and even  
30 accelerate crevice or underdeposit or other forms of localized corrosion.

As noted above, it is believed that underdeposit corrosion proceeds at a more rapid rate than does many other forms of corrosion, and continues wherever small or  
35 large volumes of a deposit remain adjacent to a surface or a pit. Hence, virtually complete removal of the products of corrosion from pits in the metal or from

otherwise corroding surfaces is especially advantageous, because of specifically minimizing or avoiding thereafter the rate of future underdeposit corrosion. Once essentially all of the products of corrosion have been removed from metallic surfaces, especially from deep pits, the rate of future corrosion can be controlled by known methods of water treatment or material selection.

Both the extent of corrosion, and the extent of corrosion removal, may be established by human visual (normal or magnified) and/or microscopic observation of component samples (often called "coupons") periodically removed from the apparatus. Electrical (or electronic) optical systems, chemical monitoring systems, pressure and differential pressure monitoring systems, flow rate and differential flow rate monitoring systems, etc., may be employed for in situ observations to supplant or supplement human observation.

An additional advantage of the above-described methods and corrosion products removal compositions is the "passivity" that is imparted to the cleaned metal surface, i.e., the subsequent initial rate of new corrosion of the surface is thereby rendered slower than that of metal cleaned by other methods and compositions.

A further advantage of the invention is that none of the ingredients of the corrosion products removal composition is on the lists of Hazardous Materials promulgated by the State of California or the U.S. Environmental Protection Agency. Of course, it is generally recognized that a fluid having a pH of 2.5 or less is for that reason classified as hazardous.

In addition to removing corrosion from metal, the compositions are useful in removing scale or deposits from plastics, ceramics, elastomers, tiles, porcelains and silica-containing glasses, such as in sight glasses of drums, overflow tanks or storage tanks. Although such materials of construction are not subject to oxidation as are iron, steel and copper, their inner surfaces in

contact with water tend to accumulate particles, or a film of deposits, stains, patinas and in situ precipitates of other contaminants in water and also fine particles of the products of oxidation. Further, some of these materials do undergo oxidation which alters the likelihood of their surfaces to attract and/or to accumulate corrosion products of iron, steel, copper, their alloys and other materials, including, but not limited to deposits, scales and generic silts. Use of the compositions described above often eliminates the need to remove from the apparatus and clean sight glasses or other system components, with the consequent interruption of service of the apparatus.

Having thus described the invention, what is claimed is:

1. A process for removing rust and other corrosion products of iron and alloys of iron, and of copper and alloys of copper, from surfaces of pipes, vessels, other fabricated apparatus and semi-fabricated metal objects, and from non-metallic surfaces, which process comprises contacting said surface with an aqueous corrosion products removal composition comprising on an anhydrous basis: in the range of from about 45 to about 75 weight % of citric acid, including partially neutralized citric acid; at least one phosphonic acid or a partially neutralized salt thereof, said phosphonic acid or salt being characterized by ability to form sequestrates or complexates with iron and/or copper; and at least one water-soluble polymeric composition, wherein at least five percent by weight of said water-soluble polymeric composition is derived from at least one of the monomers acrylic acid, methacrylic acid, maleic acid, and/or acrylamide, said water-soluble polymeric composition having a weight average molecular weight in the range from about 500 grams per mole to about 500,000 grams per mole, and is characterized by the ability to disperse particles of the products of the corrosion of iron, copper and including oxides, hydroxides and other metal derivatives as well as generic silts and the like; said composition in use being included in water in an amount of one part by anhydrous weight of said composition to in the range of about 2 to about 120 parts by weight of water, and wherein the pH of the aqueous fluid comprising said composition while in contact with said surfaces from which said rust and other corrosion products are to be removed is equal to or less than about 6.5, said contacting being continued for sufficient time to accomplish a desired degree of the removal of said rust and other corrosion products.

2. The process of claim 1 wherein said apparatus comprises part of steam generating equipment.
3. The process of claim 1 wherein said apparatus comprises part of hot water generating equipment.
- 1 4. The process of claim 1 wherein said apparatus  
2 comprises a heat exchanger.
- 1 5. The process of claim 1 wherein said apparatus  
2 comprises part of a water piping, distribution  
3 and/or storage system.
- 1 6. The process of claim 1 wherein said apparatus  
2 comprises part of a water system for a steam,  
3 electric, and/or steam electric generating power  
4 plant.
7. The process of claim 1 wherein said apparatus comprises part of crude oil producing or processing equipment, and related piping.
8. The process of claim 1 wherein said apparatus comprises an industrial, commercial or domestic tool or appliance.
9. The process of claim 1 wherein said non-metallic surface comprises glass, an elastomer, ceramic, procelain or plastic.
10. The process of claim 1 wherein said surface is being cleaned for the purpose of painting, surfacing, galvanizing or applying other protective or decorative coating.
11. The process of claim 1 wherein said phosphonic acid or salt is selected from the class consisting essentially of: 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP); diethylenetriaminepentamethylenephosphonic acid (DETPMP); ethylenediaminetetramethylenephosphonic acid (EDTMP); aminotrimethylenephosphonic acid (AMP); hexamethylenediaminetetramethylenephosphonic acid (HMDTMP); 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC); and hydroxy phosphonic acid (HPA).

12. The process of claim 1 wherein said phosphonic acid or salt is 1-hydroxy-ethylidene-1,1-diphosphonic acid (HEDP).
13. The process of claim 1 wherein said water-soluble polymeric composition is selected from the class consisting essentially of homopolymers and copolymers of the monomers acrylic acid, methacrylic acid, maleic acid, and/or acrylamide.
14. The process of claim 1 wherein said polymeric composition is polyacrylic acid.
15. The process of claim 1 wherein said water-soluble polymeric composition further comprises at least one copolymerizable additional monomer comprising at least one of an oxygen atom, a sulfur atom, a nitrogen atom or a phosphorus atom, or an alkyl group having up to 18 carbon atoms.
16. The process of claim 15, wherein said copolymerizable additional monomer is an adduct or a substituted derivative of said copolymerizable additional monomer.
17. The process of claim 1 wherein said corrosion products removal composition further comprises a corrosion inhibitor.
18. The process of claim 17 wherein said corrosion inhibitor comprises a cationic nitrogen-containing compound.
19. The process of claim 1 wherein said corrosion products removal composition is an aqueous concentrate having a pH in the range of about 3 to about 3-1/2.
20. The process of claim 1 wherein the pH of the fluid in contact with said surfaces is equal to or less than about 6.5.
21. A corrosion products removal composition adapted to be employed for removing rust and other corrosion products of iron and alloys of iron, and of copper.

and alloys of copper, from surfaces of pipes, vessels, other fabricated apparatus and semi-fabricated metal objects, which corrosion products removal composition comprises, on an anhydrous basis: in the range of from about 45 to about 75 weight % of citric acid, including partially neutralized citric acid; at least one phosphonic acid or a partially neutralized salt thereof, said phosphonic acid or salt being characterized by ability to form sequestrates or complexates with iron and/or copper; and at least one water-soluble polymeric composition, wherein at least five percent by weight of said water-soluble polymeric composition is derived from at least one of the monomers acrylic acid, methacrylic acid, maleic acid, and/or acrylamide, said water-soluble polymeric composition having a weight average molecular weight in the range from about 500 grams per mole to about 500,000 grams per mole, and is characterized by the ability to disperse particles of the corrosion of iron, copper, including oxides, hydroxides and other metal derivatives as well as generic silts and the like.

22. The composition of claim 21 wherein said phosphonic acid or salt is selected from the class consisting essentially of: 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP); diethylenetriaminepentamethylenephosphonic acid (DETPMP); ethylenediaminetetramethylenephosphonic acid (EDTMP); aminotrimethylenephosphonic acid (AMP); hexamethylenediaminetetramethylenephosphonic acid (HMDTMP); 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC); and hydroxy phosphonic acid (HPA).
23. The composition of claim 21 wherein said phosphonic acid or salt is 1-hydroxy-ethylidene-1,1-diphosphonic acid (HEDP).

24. The composition of claim 21 wherein said water-soluble polymeric composition is selected from the class consisting essentially of homopolymers and copolymers of the monomers acrylic acid, methacrylic acid, maleic acid, and/or acrylamide.
25. The composition of claim 21 wherein said polymeric composition comprises polyacrylic acid.
26. The process of claim 21 wherein said water-soluble polymeric composition further comprises at least one copolymerizable additional monomer comprising at least one of an oxygen atom, a sulfur atom, a nitrogen atom or a phosphorus atom, or an alkyl group having up to 18 carbon atoms.
27. The process of claim 26, wherein said copolymerizable additional monomer is an adduct or a substituted derivative of said copolymerizable additional monomer.
28. The composition of claim 21 wherein said corrosion products removal composition contains a corrosion inhibitor.
29. The composition of claim 28 wherein said corrosion inhibitor contains a cationic nitrogen-containing compound.
30. The composition of claim 21 wherein said corrosion products removal composition is an aqueous concentrate having a pH in the range of about 3 to about 3-1/2.
31. The composition of claim 21 wherein the corrosion products removal composition is an aqueous concentrate having a pH in the range of about 4-1/2 to less than one.
32. The composition of claim 21 further comprising sodium, potassium or ammonium hydroxide or other alkaline hydroxides.
33. A composition of claim 21, wherein the relative parts by weight of the ingredients, exclusive of water, are in the following ranges:

Citric acid and/or its salts	from about	45	to about	75
A phosphonic acid and/or its salts	from about	2	to about	15
Water-soluble polymer and/or salts thereof	from about	1-1/2	to about	8

34. A composition of claim 33, further comprising in the range from about 8 to about 11 parts by dry weight of sodium hydroxide.
35. A composition of claim 33, further comprising in the range of from about 1 to about 4 parts by weight of a corrosion inhibitor.
36. A composition of claim 33, further comprising in the range of from about 8 to about 11 parts by dry weight of sodium hydroxide or from about 11 to about 16 parts by dry weight of potassium hydroxide, and in the range of from about 1 to about 4 parts by weight of a corrosion inhibitor.
37. A corrosion products removal concentrate composition of claim 21, which composition, exclusive of water, comprises: about 58 weight percent citric acid; about 14% 1-hydroxyethylidene-1,1--diphosphonic acid (HEDP); about 4% polyacrylic acid having a molecular weight of about 2000 grams per mole; and sufficient potassium or sodium hydroxide to create a pH in the range of from about 3 to about 3-1/2 in said composition.
38. The composition of claim 37, further comprising about 2%, including any water therein, of a corrosion inhibitor.
39. A composition of claim 21, which further comprises one or more abrasives, disinfectants, odorizers,

coloring agents, viscosity modifiers and/or biocides.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/06518

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C02F 5/10, 5/14; C23G 1/02  
US CL : 252/180; 510/253, 547; 134/2, 3, 22.13, 22.14, 22.16, 22.17, 41, 42  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/180; 510/253, 547; 134/2, 3, 22.13, 22.14, 22.16, 22.17, 41, 42

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,350,536 (CHEN ET AL) 27 September 1994, abstract; col. 1, lines 46-54; col. 3, lines 64-67; col. 4, lines 1-35; col. 6, lines 1-57.	1-18, 20-29, 33, 35, 39
X	US, A, 5,259,985 (NAKANISHI ET AL) 09 November 1993, abstract; col. 2, lines 32-55; col. 3, lines 3-9, 44-55 and 66-68; col. 4, lines 1-2.	1-17, 20-28, 33, 35, 39
X	US, A, 3,463,730 (BOOTH ET AL) 26 August 1969, col. 1, lines 30-49, col. 6, lines 16-58.	1-14, 21-27, 33,
A	US, A, 3,634,257 (PORTER ET AL) 11 January 1972, see entire document.	1-39

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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*A* document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,276,185 (MARTIN) 30 June 1981, see entire document.	1-39
A	US, A, 4,802,990 (INSKEEP) 07 February 1989, see entire document.	1-39
A	US, A, 4,810,405 (WALLER ET AL) 07 March 1989, see entire document.	1-39
A	US, A 5,401,311 (FREESE ET AL) 28 March 1995, see entire document.	1-39
P	US, A, 5,445,758 (CHEN ET AL) 29 August 1995, see entire document.	1-39